An Mo Study On Modified Activated Carbons Impregnated with Metal Chlorides

On-line Number 299

Tetsuo Suzuki,* Haruhito Kodama, Shin R. Mukai, Hajime Tamon
Department of Chemical Engineering, Kyoto University, Katsura Campus, Nishikyo-ku, Kyoto 615-8510, Japan  E-mail: suzuki@cheme.kyoto-u.ac.jp

ABSTRACT

In order to obtain basic information useful for developing modified activated carbons suitable to adsorb carbon monoxide and formaldehyde, ab initio molecular orbital (MO) calculations were carried out. Adsorptive interactions between the adsorbates and modified activated carbons impregnated with metal chlorides were studied. Fragments of metal chlorides $MCl_n$ ($M$ = metal atom, $n$ = 1, 2, or 3) were adopted as molecular models of adsorption sites. Geometry optimization was done by Hartree-Fock (HF) level calculations to determine structures of adsorbates, adsorption sites, and adsorption geometries; interaction energies were evaluated by MP2 level calculations. As for CO adsorption, interaction energies were large for CuCl and PtCl$_2$, and small for chlorides of typical metal atoms. Back donation through π-bonds for CuCl and PtCl$_2$ should cause such difference. On the other hand, judging from the present calculated results, MgCl$_2$ was suitable for HCHO adsorption. Relatively small interaction energies for HCHO adsorption on CuCl and PtCl$_2$ should be partially because back-donation does not occur. In order to discuss the validity of the calculated results, several modified activated carbons impregnated with metal chlorides were prepared and adsorption experiments were carried out. Activated carbons impregnated with CuCl and PtCl$_2$ were effective in CO adsorption, one with MgCl$_2$ was effective in HCHO adsorption. The experimental results showed that the deduction based on calculated results is valid. The MO calculations seem to be applicable for the screening to select the candidate that will be effective in adsorption for a certain adsorbate.

KEY WORDS
molecular orbital theory, modified activated carbon, adsorption, computer simulation,

INTRODUCTION

Adsorption properties of modified activated carbons are discussed by using ab initio molecular orbital (MO) calculations (Daudel et. al., 1983). The MO calculations are useful to get the knowledge of microscopic features of adsorption phenomena, such as structures of adsorption sites, those of adsorbate-adsorbent systems (adsorption geometries), and adsorptive interaction energies. Such studies have been reported concerning silica surface (Pelmenschikov et. al., 1992; Sauer et. al., 1984; Suzuki et. al., 1995; Tamon et. al., 1996a; Ugliengo et. al., 1989) and zeolite (Pelmenschikov et. al., 1992). It seems possible to use the ab initio MO method for screening to select the candidate that will be effective in adsorption for a certain adsorbate.

Modification of impregnating adsorbents with metal salts is often useful to make them having desirable characteristics (Xie and Tang, 1990; Yang and Kikkinides, 1995; Yang et. al., 1996; Tamon et. al., 1996b). For example, it is well known that CuCl and AgCl, either in solution or in crystalline state, can form π-complexes with alkene (Xie and Tang, 1990). It is thus expected that we can modify adsorbents with CuCl and AgCl to have alkene selectivity. Actually, it was reported that Ag cation exchanged resins and γ-Al2O3 impregnated with CuCl show ethylene selectivity (Yang and Kikkinides, 1995).
In the present study we investigate the effectiveness of the modification of activated carbons by using various metal chlorides. Our purpose is to obtain modified carbons useful for carbon monoxide and formaldehyde elimination. Those compounds are known as representative toxic molecules for air pollution. Interaction energies between these adsorbates and adsorption sites of metal chlorides were calculated, and useful metal chlorides were deduced. Also, several modified activated carbons impregnated with metal chlorides were prepared and adsorption experiments were carried out. From the calculated and the experimental results the validity of the calculated results is discussed and suitable metal chlorides for modification are suggested.

METHODS

Computational Method

Ab initio MO calculations were carried out by using GAUSSIAN 98 program (Frisch et. al., 1998). Concerning basis sets, double zeta class basis sets are expected to be able to explain the experimental results qualitatively well for reasonable computational expense. Thus the LANL2DZ basis set, which consists of Dunning/Huzinaga valence double-zeta basis set (Dunning and Hay, 1977) on first row atoms and ECP of Hay and Wadt with double-zeta basis set (Hay and Wadt, 1985a, 1985b, Wadt and Hay, 1985) on Na-Bi atoms, was used.

In this study we treat the case that metal chlorides on the surface of activated carbon act as adsorption sites for CO and HCHO. These adsorbates are small and interact with one metal atom in metal chlorides of adsorption sites. Thus, as a first approximation, clusters consisted of one metal atom and a few chlorides, MCln (n = 1, 2, and 3), were adopted as molecular models of adsorption sites in order to discuss the adsorptive interactions.

Structures of the adsorbates, those of the adsorption sites, and the adsorption geometries were determined based on the geometry optimization method with Hartree-Fock (HF) level calculation. Schematic figures of adsorption geometries are shown for CO and HCHO adsorption on PtCl2 in Figure 1. The MP2 level calculations, in which electronic correlation was taken into account based on second-order Møller-Plesset perturbation theory (Møller and Plesset, 1934) under frozen-core conditions, were carried out in order to estimate adsorptive interaction energies ΔE. Here, ΔE is calculated by the equation:

$$\Delta E = E1 + E2 - E3$$

where E1, E2, and E3 represent the total energy of adsorbate, that of adsorption site, and that of adsorption geometry, respectively.

![Figure 1. Adsorption geometries for CO and HCHO adsorption on PtCl2 adsorption site.](image-url)
Adsorption Experiment

In order to discuss the validity of the calculated results, we prepared modified activated carbons impregnated with several metal chlorides and carried out adsorption experiments. Concerning activated carbons, Shirasagi from Takeda Chemical Industries, Ltd. (Osaka, Japan) and DARCO from Norit Japan Co., Ltd. (Tokyo, Japan) were used as supports.

Adsorption isotherms of CO at 278 K were measured by the volumetric method with BELSORP 28 (Bel Japan, Inc.). Concerning HCHO, adsorption experiments were done at 278 K using a fixed-bed column. The adsorption test column (4.2 mm in diameter, stainless steel) was packed with the modified activated carbons 40 mm in height. Sample gas, whose HCHO concentration was 70 ppm, was sent to the adsorption test column at a constant flow rate of $3 \times 10^{-5}$ m$^3$/min. The outlet gases were analyzed by gas chromatograph (GC14B, Shimadzu Co., Japan) with FID detector. Amount adsorbed for each modified carbons was evaluated by breakthrough curves.

RESULTS AND DISCUSSION

Calculated Results

Interaction energies $\Delta E$ were calculated for CO and various metal chlorides, and some results are shown in Table 1.

<table>
<thead>
<tr>
<th>Metal chlorides</th>
<th>MgCl$_2$</th>
<th>CrCl$_3$</th>
<th>CoCl$_2$</th>
<th>NiCl$_2$</th>
<th>CuCl</th>
<th>ZnCl$_2$</th>
<th>SnCl$_2$</th>
<th>PtCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>39.6</td>
<td>84.3</td>
<td>63.5</td>
<td>58.8</td>
<td>142.3</td>
<td>35.7</td>
<td>22.3</td>
<td>237.0</td>
</tr>
</tbody>
</table>

It can be seen that values of $\Delta E$ for PtCl$_2$ and CuCl are large enough to expect that these chlorides act as effective adsorption sites for CO. The reason of the large $\Delta E$ should be that CO adheres to Pt or Cu with both $\sigma$-bonds and $\pi$-bonds, and that back-donation occurs through the $\pi$-bonds to stabilize those metal chlorides-CO complexes. On the contrary, $\Delta E$ tends to take small values for chlorides of typical metal atoms. This suggests that those chlorides are not effective in CO adsorption.

![Figure 2. Schematic figure of back-donation. Arrows indicate directions of electron transfer.](image)

Calculations were also carried out for interactions between HCHO and several metal chlorides. Main results are listed in Table 2. Though $\Delta E$ takes large values for CuCl and PtCl$_2$, these values are less than those for CO adsorption. It was found that back-donation does not occur between HCHO and CuCl or PtCl$_2$, a fact which is the reason of appearance of relatively weak interaction between HCHO and those...
metal chlorides. Large ∆E values were also obtained for typical metal atoms, such as MgCl₂. These large values seem to be derived from quite large negative charges on O atom of HCHO.

Table 2. ∆E values for HCHO [kJ/mol]

<table>
<thead>
<tr>
<th>Metal chlorides</th>
<th>MgCl₂</th>
<th>CrCl₂</th>
<th>CoCl₂</th>
<th>NiCl₂</th>
<th>CuCl</th>
<th>ZnCl₂</th>
<th>SnCl₂</th>
<th>PtCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>∆E</td>
<td>100.4</td>
<td>117.5</td>
<td>95.7</td>
<td>91.8</td>
<td>113.4</td>
<td>70.8</td>
<td>66.8</td>
<td>123.7</td>
</tr>
</tbody>
</table>

Experimental Results

Modified activated carbons impregnated with metal chlorides, which appears in the above two tables, were prepared and adsorption experiments were carried out. The CO adsorption isotherms for modified activated carbons are shown in Figure 3. It can be seen that CO is much adsorbed on activated carbons impregnated with CuCl and PtCl₂. For example, at 0.006 relative pressure (101 kPa equilibrium pressure), the amount of CO adsorbed on the carbon with CuCl is about 4 times as much as that on commercial one. On the contrary, amount adsorbed for other modified activated carbons is almost the same or less than that of commercial one; only the carbon with CrCl₂ shows a small increase in CO amount adsorbed compared with the commercial one. These results agree well with our expectation deduced from the calculated results.

Figure 3. CO adsorption isotherms at 298 K.
In Table 3, HCHO amount adsorbed on several modified activated carbons are listed. It can be seen that HCHO amount adsorbed for the activated carbon impregnated with MgCl\(_2\) is greater than those with PtCl\(_2\) and CuCl. Again, these results agree well with our speculation according to the calculated results.

<table>
<thead>
<tr>
<th>Metal chlorides</th>
<th>MgCl(_2)</th>
<th>CrCl(_2)</th>
<th>CoCl(_2)</th>
<th>NiCl(_2)</th>
<th>CuCl</th>
<th>ZnCl(_2)</th>
<th>SnCl(_2)</th>
<th>PtCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount adsorbed</td>
<td>16.8</td>
<td>3.67</td>
<td>10.0</td>
<td>2.59</td>
<td>0.50</td>
<td>0.70</td>
<td>2.54</td>
<td>4.24</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In this study the adsorption characteristics of the modified activated carbons with several metal chlorides have been discussed by using the ab initio MO method. From the calculated results we could deduce that the activated carbons impregnated with CuCl and PtCl\(_2\) are effective in CO adsorption, and the carbon with MgCl\(_2\) is effective in HCHO adsorption. The validity of this deduction was confirmed by the experiment with the modified activated carbons.

It is difficult to estimate the interaction energy quantitatively well, and the interaction energy is only one of several factors that determine the characteristics of an adsorbent. However, in the present case we have succeeded in predicting a character of a novel adsorbent. It seems thus useful to apply the ab initio MO method to screening for development of adsorbent. Reduction of computational expense of the ab initio MO method due to development of computers and computational chemistry will enable us to modify and design desirable adsorbents more easily.

**ACKNOWLEDGMENT**

The authors acknowledge the Supercomputer Laboratory of the Institute for Chemical Research in Kyoto University and the Data Processing Center of Kyoto University for their generous permission to use their computers.

**REFERENCES**


